

# SCIENCE FOR CERAMIC PRODUCTION

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## BINDERS BASED ON AQUEOUS DISPERSIONS OF POLYMERS FOR PLASTIC SHAPING OF CERAMIC PRODUCTS

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Some special features of the deformation behavior of plastic corundum mixtures and semifinished products with temporary technological binders based on aqueous dispersions of polyvinyl acetate and polymethyl acrylate are considered. As compared to conventional binders, the new binders widen the range of the plastic state of the mixtures with preservation of a high level of molding properties and make it possible to increase the strength of molded preforms. It is shown that the binders are applicable for shaping articles from narrow-fractionated powders.

Plastic molding is an intensely developed method for fabricating ceramic semifinished products, especially if they are of complex configuration. The method has some advantages over other shaping techniques but the requirements for the properties of the molding mixtures are more rigorous. For this reason, the choice of the temporary technological binder (TTB) is a very important factor. Multicomponent binders of various natures have become popular recently, including aqueous suspensions of polymers and latexes [1–3]. However, publications in this field are quite scarce and are mainly limited to patent information (for example, USSR Inventor's Certificates 1147705, 1428743, 682477, Patent 225941 GDR, Application 333069 Japan) which does not contain a description of the properties of the mixture and the semifinished products produced with use of the binders.

Since latexes and aqueous dispersions of polymers are a novel kind of binder in the Russian ceramics industry, it seems expedient to give a short description of these products.

In contrast to the traditionally used solutions of high-molecular-weight substances, polymer dispersions and latexes are binary or multiphase systems. The disperse phase is polymer particles synthesized by the method of emulsion polymerization, stabilized by emulsifiers and protective colloids (surfactants or electrolytes), and distributed in an aqueous dispersion medium. Hydrocarbon radicals of asymmetric amphiphilic molecules of the SF are pulled into the surface layer of the polymer particles and the polar groups point to the aqueous phase. The main part of the emulsifier is

adsorbed on the surface of the interphase boundary and a small fraction is present in the volume of the dispersion medium [4].

Polymer dispersions are characterized by the features of the colloidal state of the disperse system, namely, small size of the particles that ranges between 10 and 100 nm for latexes, high aggregate stability caused by the existence of a electric double or adsorption layer of SF on the surface of the polymer particles. The structure and properties of this layer are determined by the special features of the interaction between the particles themselves and between the particles and other components of the molding mixture. The rheological properties of polymer dispersions can be varied by changing the nature and concentration of the protective colloids or emulsifiers [5, 6]. The use of polymer dispersions and latexes is connected with interaction and coagulation of polymer particles and the transition of the system from a colloidal-disperse state into the macrostate of block, gel, sponge, film, etc.

The uniqueness of the colloid chemical properties of polymer dispersions is caused by a combination of special features inherent in emulsions, sols and suspensions. A high concentration of aggregates of macromolecules with considerable deformability and the presence of a layer of emulsifier on their surface relate such systems to emulsions. At the same time, the aggregates of macromolecules are disperse solid-like particles with restricted mobility, like the disperse component of lyophobic hydrosols and suspensions. Aqueous dispersions and latexes differ from structurized polymer

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solutions by the low viscosity and high content of polymer [7].

The special features of the structure of aqueous dispersions of polymers and latexes allow us to assume that the properties of the ceramic molding mixtures and preforms based on them will differ considerably from the properties of semifinished products produced with the use of traditional solutions.

In the present work we considered the effect of the composition of binders based on aqueous polymer dispersions on the properties of corundum molding mixtures and semifinished products. The disperse phase was commercial alumina G-00 with additives of polishing electrocorundum powders M-10 and M-14 used for diminishing the effect of the polydispersity of the solid phase.

The temporary technological binders were a polyvinyl acetate dispersion (PVAD) and polymethyl acrylate in the form of Lacporol-203 latex that contained butyl acrylate, methyl acrylate and methacrylic acid in addition to the main component. The initial mass fraction of polymers in the binders was 45%. It was changed by evaporating and diluting the initial polymer dispersion. For comparison we used aqueous solutions of carboxymethyl cellulose (CMC), methyl cellulose (MC), and polyvinyl alcohol (PVC) with 3 wt.% MC, 6 wt.% CMC, and 6 wt.% PVC.

The rheological characteristics of the molding mixtures were determined from the curves describing the development of deformation under shear loads (shear stresses) with calcu-

lation of the moduli of rapid and delayed reversible deformations, plastic viscosity, yield strength  $P_k$ , and deformation criteria, i.e., elasticity  $\lambda$ , relaxation time  $\theta$ , and Volarovich plasticity  $Pl$ . In addition we plotted the diagrams of deformation development according to C. P. Nichiporenko and calculated the total deformation power  $E_s$  and the proportion of rapid ( $\varepsilon_1$ ), delayed ( $\varepsilon_2$ ) reversible and plastic ( $\varepsilon_3$ ) deformations [8]. The drying shrinkage of the specimens was calculated from the proportion of the density of the mixture to that of the air-dried semifinished product determined by hydrostatic weighing of paraffined specimens [9].

In order to estimate the range of the plastic state  $WIP$ , the ultimate yield and spreading strength  $W_s$ , and the optimum molding moisture content  $W_m$  we used the method of representing the dependence of the plastic strength according to P. A. Rebinder  $P_m$  on the content of binder  $W$  in semilogarithmic coordinates [10],

$$\log P_m = A - BW, \quad (1)$$

where  $A$  and  $B$  are empirical constants.

The dependence of the plastic strength on the content of the binder is described adequately by this equation (Table 1). An exception is the mixtures based on alumina with 54% Lacropol in the binder, for which the calculated yield point has a negative value, which indicates that the plastic strength changes little with the content of the binder in the region of the plastic state. For mixtures of narrow-fractionated electrocorundum powders, the nature of the binder based on the considered polymer solutions virtually does not affect the parameters of Eq. (1), and the dependence  $P_m(W)$  can be represented by a generalizing equation with a high value of the correlation coefficient  $r$ .

In accordance with the classification used for clays, mixtures based on alumina and containing polymer solutions

TABLE 1

Binder	Content, %, in the binder	<i>A</i>	<i>B</i>	<i>r</i>	$W_s$ , %	$W_m$ , %	$WIP$
Mixtures based on alumina							
KMC	6	5.67	0.102	0.95	33.9	38.2	14.0
PVC	6	5.56	0.113	0.99	29.8	33.7	12.7
MC	3	5.09	0.093	0.95	31.2	15.6	36.0
Lacropol	34	3.72	0.050	0.95	28.8	28.0	37.5
Lacropol	45	2.52	0.021	0.86	12.1	69.0	33.7
Lacropol	54	4.90	0.011	0.63	-35.1	5.3	129.9
PVA	35	3.64	0.030	0.98	45.4	46.3	60.0
PVA	45	2.91	0.021	0.99	30.0	67.0	50.7
PVA	54	5.94	0.032	0.96	20.4	33.8	43.1
Mixtures based on corundum M-14							
KMC, MC and PVC*	6	15.20	0.465	0.84	21.4	22.4	3.0
Lacropol	45	8.63	0.124	0.96	27.1	0.6	11.3
PVA	45	8.24	0.109	0.98	27.1	31.1	12.8
Mixtures based on corundum M-10							
KMC, MC and PVC*	6	9.09	0.204	0.87	18.7	20.8	6.9

\* Averaged values.

TABLE 2

Binder	Content, %, in the binder	$E_m$ , kPa	$\lambda$	0. sec	$P_k$ , kPa	$Pl$ , $10^{-6}$ $\text{sec}^{-1}$	$E_s$ , kPa
Mixtures based on alumina							
Lacropol	34	34	0.611	648	-0.03	-3.36	2.51
Lacropol	45	208	0.496	570	-0.04	-0.844	14.5
Lacropol	54	104	0.666	466	-0.01	-0.433	7.08
PVA	34	69	0.617	432	-0.006	-0.465	4.47
PVA	45	37	0.721	1169	0.07	3.07	3.18
PVA	54	44	0.964	34	0.004	0.946	2.17
PVC	6	180	0.895	1426	0.01	0.358	16.89
KMC	6	200	0.545	244	0.03	1.31	9.95
MC	3	405	0.252	1275	46.68	1.72	40.5
Mixtures based on corundum M-14							
Lacropol	45	91	0.473	1215	-3.5	-0.08	75.6
PVA	45	66	0.425	1027	-0.3	-1.11	53.5

TABLE 3

Binder	Content, %		Coordinates of points, %			Structural-mechanical type
	in binder	in mixture	$\varepsilon_1$	$\varepsilon_2$	$\varepsilon_3$	
Mixtures based on alumina						
Lacropol	45	90	35	34	30	0
Lacropol	34	60	28	45	27	1
Lacropol	54	150	23	45	32	2
PVA	45	100	23	61	15	1
PVA	34	60	25	40	35	1
PVA	54	150	2	48	51	2
PVC	6	35	10	84	6	1
KMC	6	40	23	27	50	2
MC	3	37	75	25	> 1	0
Mixtures based on corundum M-14						
Lacropol	45	35	44	39	17	0
PVA	45	35	47	34	19	0

should be classified as moderately plastic; mixtures based on grinding corundum powders have low plasticity. The use of aqueous dispersions of polymers provides for high plasticity (the plasticity number exceeds 30%) of alumina-based mixtures and moderate plasticity of mixtures from grinding corundum powders (the region of the plastic state is about 70%). At the same time, we should note that the content of polymer dispersions in the mixtures exceeds that of conventional binders.

Table 2 presents the deformation properties of mixtures based on alumina determined at binder contents close to optimum. Mixtures based on polymer dispersions are characterized by high elasticity that commonly increases with an increase in the concentration of the polymer dispersion and by a low total deformation modulus  $E_m$ . The specific features of the structure of the polymer dispersions cause low, almost zero, values of the yield strength and, as a consequence, low Volarovich plasticity, i.e., the moistened semifinished product possesses a comparably low capacity to preserve the shape. The increase in the grain size of the solid phase in the transition from alumina to grinding powders does not influence these parameters but increases substantially (by a factor of 5–10) the total power of deformation and the relaxation time, which diminishes spoilage in the early drying stages and in transporting moistened preforms.

The proportion of deformations in the considered mixtures is such that deformation development in them is uniform independently of the dispersion of the solid phase, in contrast to mixtures that contain structurized polymer solutions. The proportion of Nichiporenko deformations at a moisture content close to the optimum molding value is presented in Table 3.

The density of mixtures and air-dried semifinished products is preserved at the level of the density of mixtures based

TABLE 4

Binder	Rupture strength, MPa	Elongation, %
PVAD	15.2	5–20
Lacropol	1.7	10–100
KMC	0.2	*
MC	0.3	"
PVC	0.5	"

\* No elongation before failure.

on traditional binders or somewhat exceeds the latter, despite the elevated content of binder in the mixture, i.e., is determined predominantly by the special features of packing of the particles of solid phase. The volume air shrinkage of the preforms at binder contents close to the optimum value does not exceed 10% and is independent of the nature of the binder, but increases with an increase in its content.

The special features of preforms based on aqueous dispersions of polymers consist in the change of the fracture behavior from brittle to plastic, high values of the rupture strength, and considerable (up to 5–10%) elongation (Table 4).

Thus, the use of aqueous dispersions of polymers as the main component of temporary technological binder widens the region of the plastic state of the molding mixtures, diminishes considerably the dependence of their properties on the grain composition, and improves the strength and deformation characteristics of air-dried preforms.

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